Supporting Information

BaF_2:$Eu^{2+/3+}$, Tb^{3+} nanofibres achieve enhanced multicolor luminescence and white-light emission *via* multi-channel excitation and energy migration procedure

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Chemicals and characterization methods

Barium acetate [$Ba(CH_3COO)_2$, AR],europium oxide (Eu_2O_3, 99.99%), terbium oxide (Tb_4O_7, 99.99%), polyvinylpyrrolidone (PVP, K90, MW=1300000) were purchased from Aladdin Reagent Co., Ltd. *N, N*-dimethylformamide (DMF, AR) and ammonium hydrogen difluoride (NH_4HF_2, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Activated carbon granules were bought from Tianjin Guangfu Technology Development Co., Ltd. Concentrated nitric acid (HNO_3, AR) was purchased from Beijing Chemical Works. Deionized water was homemade. All chemicals were directly used as received without further purification.

X-ray diffraction (XRD) data were collected on a Rigaku D/max-RA x-ray diffractometer made by Bruker corporation with the model of D8 FOCUS and Cu Kα radiation. The operation current and voltage were maintained at 20 mA and 40 kV, respectively. The scanning speed, the step length and the diffraction range were set to 10 $°\cdot min^{-1}$, 0.1 ° and 10-80 °, respectively. The size and morphology of the samples were observed by a JSM-7610F field-emission scanning electron microscope (FESEM) made by JEOL Company. The elemental analysis was performed by an energy-dispersive spectroscopy (EDS, X-MaxN80) attached to the FESEM.An X-ray photoelectron spectroscopy (XPS, PHI 5500 Versa Probe) was used to obtain the surface element compositions and valence states of samples, the full spectrum scan was ranged from 0 to 1200 eV.

A Hitachi fluorescence spectrophotometer (F-7000) was utilized to accomplish the luminescent analysis of the samples (measurement conditions: EX slit: 5.0 nm; EM slit: 5.0 nm; Current:1 A; Voltage:700 V). High voltage DC power supply (DW-P303-1ACDF0) was purchased from Tianjin Dongwen High Voltage Power Supply Corp. (Tianjin, China). Programmable high-temperature furnace (KSL-1400X-A2) was bought from Hefei Kejing Materials Technology Co., Ltd. (Hefei, China).

Table S1 Ingredient and detailed dosage of spinning liquids for preparing nanofibrous samples

Samples	**Spinning liquids**				
	$Ba(CH_3COOH)_2$/g	**Eu_2O_3/g**	**Tb_4O_7/g**	**DMF/g**	**Deionized water/g**
BaF_2:2%$Eu^{2+/3+}$ nanofibres	1.1685	0.0164	0	2.5333	5.0667
BaF_2:4%$Eu^{2+/3+}$ nanofibres	1.1373	0.0326	0	2.5333	5.0667
BaF_2:6%$Eu^{2+/3+}$ nanofibres	1.1066	0.0487	0	2.5333	5.0667
BaF_2:8%$Eu^{2+/3+}$ nanofibres	1.0762	0.0645	0	2.5333	5.0667
BaF_2:10%$Eu^{2+/3+}$ nanofibres	1.0459	0.0801	0	2.5333	5.0667
BaF_2:12%$Eu^{2+/3+}$ nanofibres	0.9692	0.0910	0	2.5333	5.0667
BaF_2:14%$Eu^{2+/3+}$ nanofibres	0.9344	0.1048	0	2.5333	5.0667
BaF_2:10%Tb^{3+} nanofibres	1.0024	0	0.08151	2.5333	5.0667
BaF_2:10%$Eu^{2+/3+}$, 2%Tb^{3+} nanofibres	0.9687	0.0758	0.0161	2.5333	5.0667
BaF_2:10%$Eu^{2+/3+}$, 4%Tb^{3+} nanofibres	0.9334	0.0748	0.0318	2.5333	5.0667
BaF_2:10%$Eu^{2+/3+}$, 6%Tb^{3+} nanofibres	0.8991	0.0737	0.0470	2.5333	5.0667
BaF_2:10%$Eu^{2+/3+}$, 8%Tb^{3+} nanofibres	0.8658	0.0727	0.0618	2.5333	5.0667
BaF_2:10%$Eu^{2+/3+}$, 10%Tb^{3+} nanofibres	0.8333	0.0718	0.0762	2.5333	5.0667
BaF_2:10%$Eu^{2+/3+}$, 12%Tb^{3+} nanofibres	0.8017	0.0708	0.0903	2.5333	5.0667
BaF_2:10%$Eu^{2+/3+}$, 14%Tb^{3+} nanofibres	0.7709	0.0698	0.1039	2.3333	5.6667

Fabrication of BaF_2:10%Tb^{3+} nanofibres

The processes for preparing the BaF_2:10%Tb^{3+} nanofibres were the same as those for preparing the BaF_2:$Eu^{2+/3+}$nanofibres depicted in the Section 2.2. The detailed dosages of spinning liquids for preparing BaF_2:10%Tb^{3+} nanofibres were summarized in Table S1.

The XRD patterns of BaF_2:10%Tb^{3+} nanofibres are given in Fig. S1. All diffraction peaks correspond to BaF_2 standard cards (PDF#85-1341), meaning that pure-phase BaF_2:10%Tb^{3+} nanofibres are obtained.

Table S2 Lattice constants and cell volumes of BaF_2:x%$Eu^{3+/3+}$, y%Tb^{3+} nanofibres and PDF standard card data of BaF_2

Samples	Lattice constant a(Å)	Lattice constant b(Å)	Lattice constant c(Å)	Cell volume ($Å^3$)
BaF_2:2%$Eu^{2+/3+}$ nanofibres	6.193	6.193	6.193	237.522
BaF_2:4%$Eu^{2+/3+}$ nanofibres	6.184	6.184	6.184	236.488
BaF_2:6%$Eu^{2+/3+}$ nanofibres	6.179	6.179	6.179	235.914
BaF_2:8%$Eu^{2+/3+}$ nanofibres	6.174	6.174	6.174	235.342
BaF_2:10%$Eu^{2+/3+}$ nanofibres	6.169	6.169	6.169	234.771
BaF_2:12%$Eu^{2+/3+}$ nanofibres	6.164	6.164	6.164	234.201
BaF_2:14%$Eu^{2+/3+}$ nanofibres	6.159	6.159	6.159	233.631
BaF_2:10%$Eu^{2+/3+}$, 2%Tb^{3+} nanofibres	6.078	6.078	6.078	224.534
BaF_2:10%$Eu^{2+/3+}$, 4%Tb^{3+} nanofibres	6.059	6.059	6.059	222.435
BaF_2:10%$Eu^{2+/3+}$, 6%Tb^{3+} nanofibres	6.045	6.045	6.045	220.897
BaF_2:10%$Eu^{2+/3+}$, 8%Tb^{3+} nanofibres	6.041	6.041	6.041	220.458
BaF_2:10%$Eu^{2+/3+}$, 10%Tb^{3+} nanofibres	6.031	6.031	6.031	219.365
BaF_2:10%$Eu^{2+/3+}$, 12%Tb^{3+} nanofibres	6.027	6.027	6.027	218.929
BaF_2:10%$Eu^{2+/3+}$, 14%Tb^{3+} nanofibres	6.022	6.022	6.022	218.385
BaF_2 Standard card data	6.196	6.196	6.196	237.867

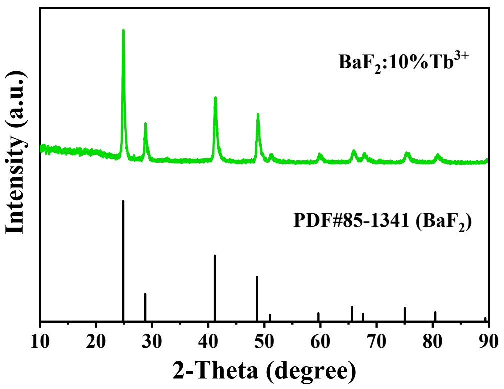

Fig. S1 XRD patterns of BaF$_2$:10%Tb^{3+} nanofibres with PDF standard card of BaF$_2$.

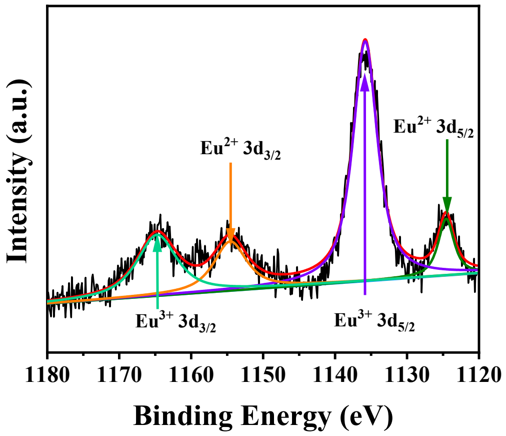

Fig. S2 XPS spectra of Eu 3d in the BaF$_2$:10%Eu$^{2+/3+}$ nanofibres stored for nine months.

Table S3 Contents of Eu^{2+} and Eu^{3+} in BaF$_2$:x%Eu$^{2+/3+}$ nanofibres stored for nine months

Samples	Eu^{2+} (3d$_{3/2}$+3d$_{5/2}$) (%)	Eu^{3+} (3d$_{3/2}$+3d$_{5/2}$) (%)	Eu^{2+}/Eu^{3+} (molar ratio)
BaF$_2$:10%Eu$^{2+/3+}$	18.96	81.04	0.30:1

The diameters of 100 fibres are measured and the histogram of diameters distribution is drawn by using the Origin software, as shown in the Fig. S3.

Fig. S4 indicates the EDS spectra of the samples. Elemental C, N, O, Eu and Ba are found in PVP/[Ba(CH$_3$COO)$_2$+10%Eu(NO$_3$)$_3$]composite nanofibres (Fig. S4a). After calcination, N and O elements disappear and F element appears in the BaF$_2$:10%Eu$^{2+/3+}$ nanofibres (Fig. S4c). Similar experimental results also exist in PVP/[Ba(CH$_3$COO)$_2$+10%Eu(NO$_3$)$_3$+10%Tb(NO$_3$)$_3$] composite nanofibres and BaF$_2$:10%Eu$^{2+/3+}$, 10%Tb^{3+} nanofibres (Fig. S4b and S4d). In addition to the above elements, Tb element is also found, which is consistent with the sample composition. The existence of elemental C is due to the presence of carbon in the conductive adhesive during the test and the incomplete volatilization of a small amount of polymer during the high-temperature calcination process. The appearance of F element proves that F ion is successfully introduced into the samples during fluorination process. The emergence of Eu and Tb elements proves that rare earth elements have been successfully doped. There are no other impure elements in the above samples, meaning that the samples with high purity are obtained.

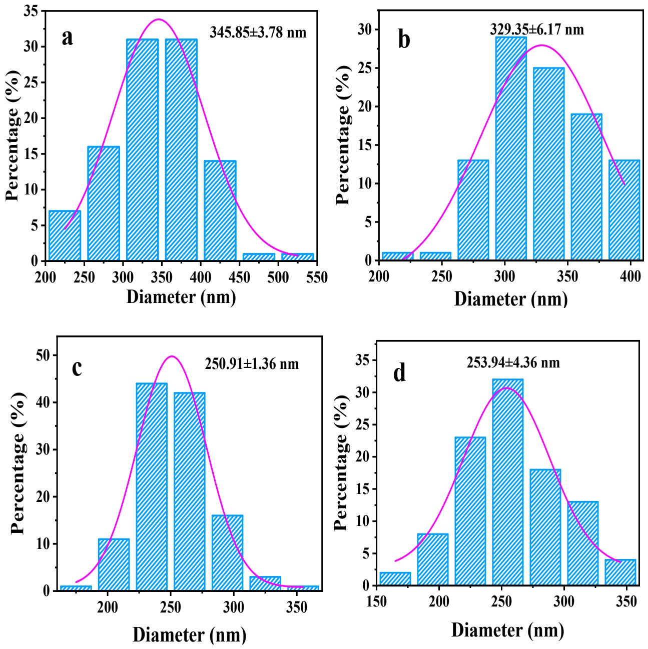

Fig. S3 Histograms of diameters distribution of PVP/[Ba(CH_3COO)$_2$+10%Eu(NO_3)$_3$] composite nanofibres (a), PVP/[Ba(CH_3COO)$_2$+10%Eu(NO_3)$_3$+10%Tb(NO_3)$_3$] composite nanofibres (b), BaF_2:10%$Eu^{2+/3+}$ nanofibres (c)and BaF_2:10%$Eu^{2+/3+}$, 10%Tb^{3+} nanofibres (d).

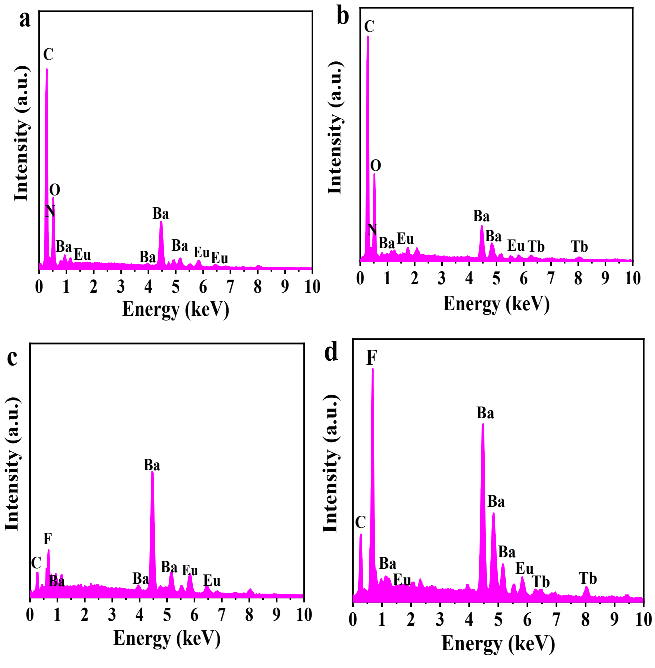

Fig. S4 EDS spectra of PVP/[Ba$(CH_3COO)_2$+10%Eu$(NO_3)_3$] composite nanofibres (a), PVP/[Ba$(CH_3COO)_2$+10%Eu$(NO_3)_3$+10%Tb$(NO_3)_3$] composite nanofibres (b), BaF_2:10%$Eu^{2+/3+}$nanofibres (c) and BaF_2:10%$Eu^{2+/3+}$, 10%Tb^{3+} nanofibres (d).

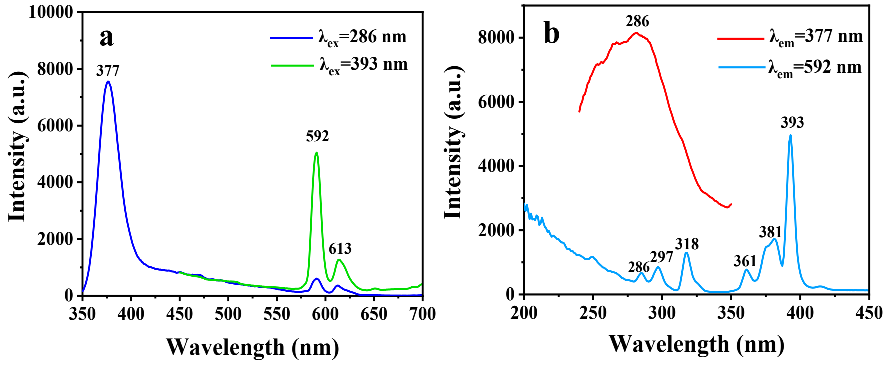

Fig. S5 Emission (λ_{ex}=286, 393 nm) (a) and excitation (λ_{em}=377, 592 nm) (b) spectra of BaF_2:10%$Eu^{2+/3+}$ nanofibres.

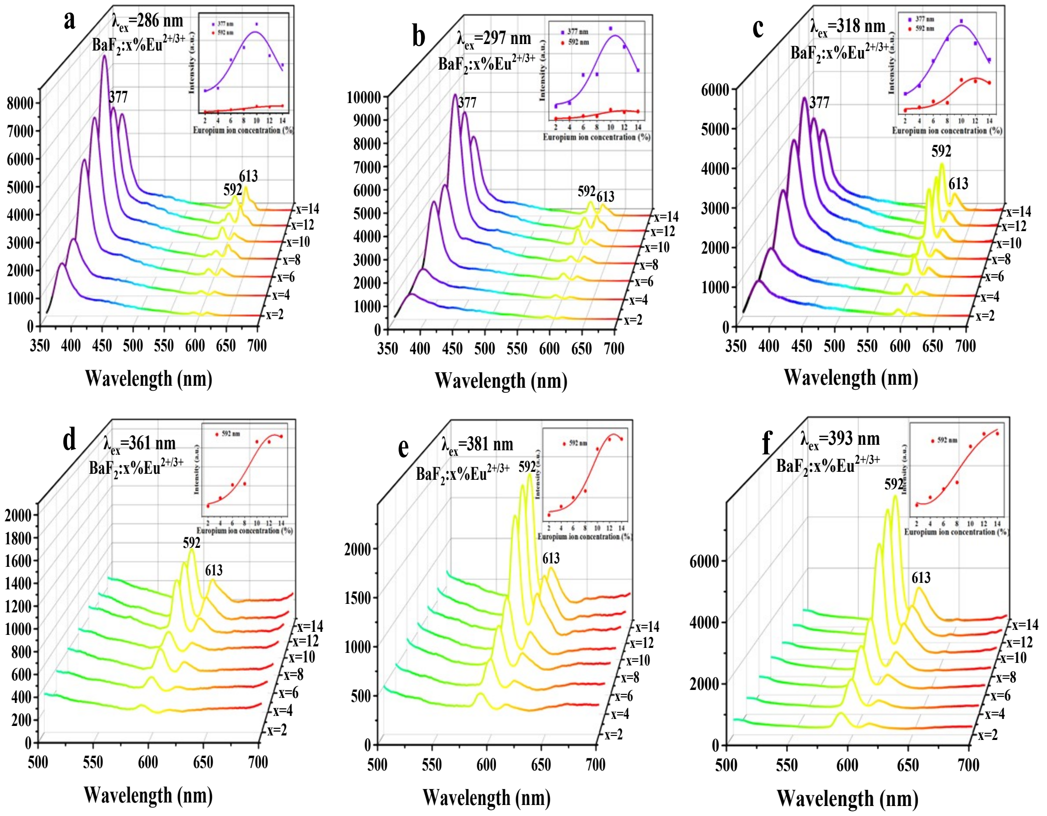

Fig. S6 Emission spectra of BaF_2:x%$Eu^{2+/3+}$ nanofibres (x=2, 4, 6, 8, 10, 12, 14) under different wavelengths ultraviolet (UV) light excitation of 286 nm (a), 297 nm (b), 318 nm (c), 361 nm (d), 381 nm (e) and 393 nm (f); Inserts: dependence of the emission intensity at 377 and 592 nm on europium ion doping concentration under different wavelengths ultraviolet (UV) light excitation.

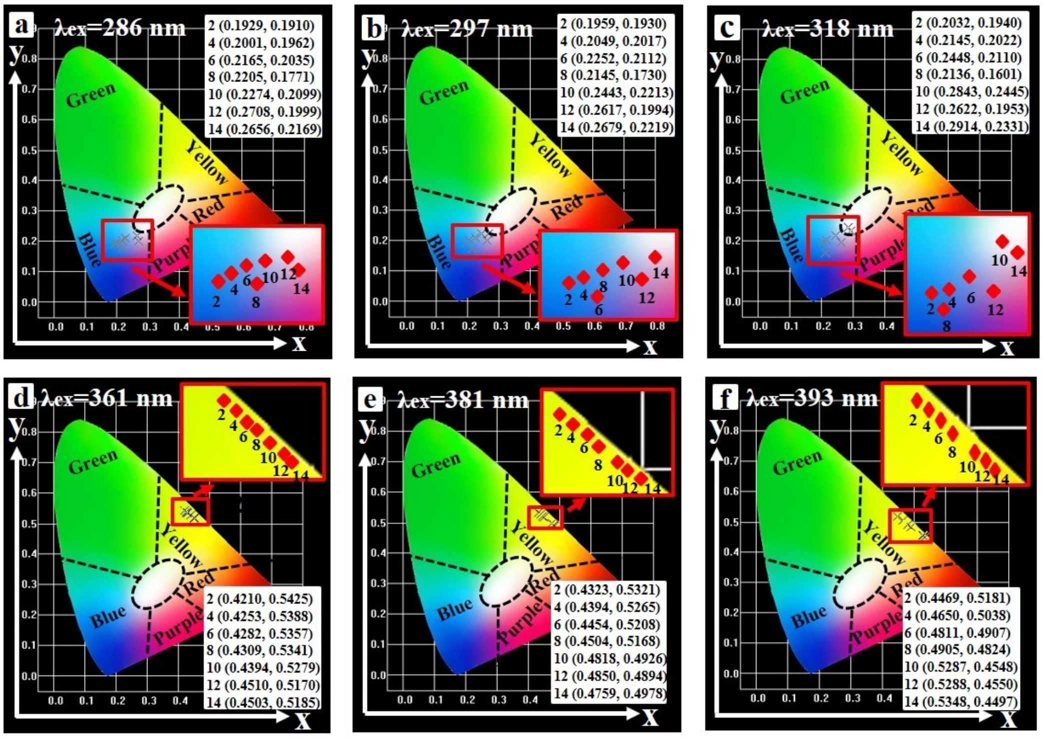

Fig. S7 CIE chromaticity coordinates diagrams for BaF$_2$:x%Eu$^{2+/3+}$ (x=2, 4, 6, 8, 10, 12, 14) nanofibres at excitation wavelengths of 286 nm (a), 297 nm (b), 318 nm (c), 361 nm (d), 381 nm (e) and 393 nm (f).

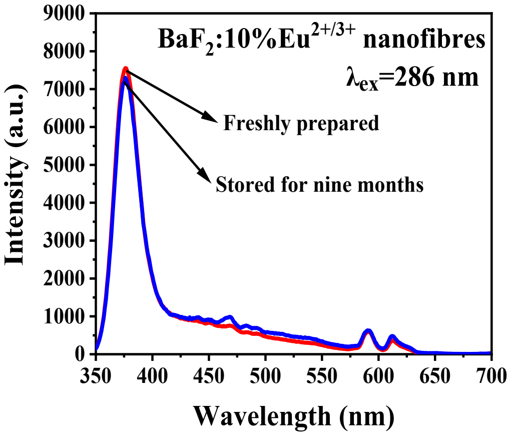

Fig. S8 Emission spectra of BaF$_2$:10%Eu$^{2+/3+}$ nanofibres freshly prepared and stored for nine months under 286-nm UV light excitation.

Stability study

For researching the stability of the samples, XPS spectra and emission spectra of BaF$_2$:10%Eu$^{2+/3+}$ nanofibres freshly prepared and stored for nine months are determined and comparatively shown in Fig. S2 and Fig. S8. For the two samples, the XPS peaks of Eu are located at 1124.8 eV (Eu^{2+} $3d_{5/2}$), 1135.0 eV (Eu^{3+} $3d_{5/2}$), 1154.4 eV (Eu^{2+} $3d_{3/2}$) and 1164.2 eV (Eu^{3+} $3d_{3/2}$), as indicated in Fig. S2. No significant change in the positions of the XPS peaks is found. Simultaneously, the luminous intensity is also not significantly reduced after storage for 9 months (Fig. S8). The above findings prove that the valence state and existence form of Eu in BaF_2 nanofibres can stay in the air for a long time, and the samples have excellent stability.